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(54) Title: LAUNDRY DETERGENT COMPOSITIONS WITH CELLULOSE POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS LAUNDERED THEREWITH			
(57) Abstract			
<p>Disclosed are detergent compositions and methods which utilize certain modified cellulose ethers as fabric treatment agents that can impart fabric appearance and integrity benefits to fabrics and textiles laundered in washing solutions which contain such agents. Such modified cellulose ether fabric treatment agents are those having selected types and amounts of anhydroglucoside ring substituents in order to render them nonionic, cationic or anionic in nature.</p>			

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LAUNDRY DETERGENT COMPOSITIONS WITH CELLULOSEC POLYMERS  
TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS  
LAUNDERED THEREWITH

TECHNICAL FIELD

The present invention relates to heavy duty laundry detergent compositions, in either liquid or granular form, which contain certain types of modified cellulose ether materials to impart appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

BACKGROUND OF THE INVENTION

It is, of course, well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye from fabrics and textiles.

and impart a faded, worn out appearance as a result of diminished color intensity, and in many cases, as a result of changes in hues or shades of color.

Given the foregoing, there is clearly an ongoing need to identify materials which could be added to laundry detergent products that would associate themselves with the fibers of the fabrics and textiles laundered using such detergent products and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance. Any such detergent product additive material should, of course, be able to benefit fabric appearance and integrity without unduly interfering with the ability of the laundry detergent to perform its fabric cleaning function. The present invention is directed to detergent compositions containing certain types of cellulosic materials that perform in this desired manner.

### SUMMARY OF THE INVENTION

The laundry detergent compositions herein comprise from about 1% to 80% by weight of a detergentsurfactant, from about 0.1% to 80% by weight of an organic or inorganic detergency builder and from about 0.1% to 8% by weight of certain types of modified cellulose ether fabric treatment agents. The detergentsurfactant and detergency builder materials can be any of those useful in conventional laundry detergent products. The modified cellulose ether materials are those which have a molecular weight of from about 10,000 to 2,000,000 and are comprised of repeating substituted anhydroglucose units corresponding to the general Structural Formulas Nos. I, II and III set forth hereinafter in the "Detailed Description of the Invention" section. (In the Structural Formulas hereinafter set forth, substituents are shown in specific positions on the anhydroglucose rings which repeat to form the substituted cellulose ether polymers. It should be understood that this is for illustration purposes only and that such substituents may be found on any of the carbon atoms of the anhydroglucose rings.)

One useful type of cellulose ethers comprises hydrophobically-modified, nonionic materials with anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. Ring substituents are alkoxyLATED in amounts ranging from about 1 to 20 moles.

A second useful type of cellulose ether comprises cationic cellulose ether materials which may have anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. Anhydroglucose ring substituents

contain from about 1 to 20 moles of alkoxylation and from about 0.005 to 0.5 moles of quaternary ammonium cationic moieties.

A third type of cellulose ether comprises anionic cellulose ether materials which may have anhydroglucose ring alkyl substitution ranging from about 0.1% to 5% by weight of the cellulose ether. The anhydroglucose rings in such anionic materials also have a degree of carboxymethyl substitution ranging from about 0.05 to 2.5. Combinations of the nonionic, cationic and anionic modified cellulose ethers can also be employed.

In its method aspect, the present invention relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions described herein, or formed from the individual components of such compositions. Laundering of fabrics and textiles in such washing solutions, followed by rinsing and drying, imparts fabric appearance benefits to the fabric and textile articles so treated. Such benefits can include improved overall appearance, pill/fuzz reduction, antifading, improved abrasion resistance, and/or enhanced softness.

#### DETAILED DESCRIPTION OF THE INVENTION

As noted, the laundry detergent compositions of the present invention essentially contain detergentsurfactant, detergent builder and certain modified cellulose ether fabric treatment agents which serve to enhance fabric appearance and integrity upon use of the detergent compositions to launder fabrics and textiles. Each of these essential detergent composition components, as well as optional ingredients for such compositions and methods of using such compositions, are described in detail as follows: All percentages and ratios given are by weight unless other specified.

##### A) Detergent Surfactant

The detergent compositions herein essentially comprise from about 1% to 80% by weight of a detergentsurfactant. Preferably such compositions comprise from about 5% to 50% by weight of this surfactant. Detergentsurfactants utilized can be of the anionic, nonionic, zwitterionic, ampholytic or cationic type or can comprise compatible mixtures of these types. Detergentsurfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905,

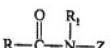
Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference. Of all the surfactants, anionics and nonionics are preferred.

Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkyloammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional non-soap anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, and ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are a) the sodium, potassium and ammonium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-C<sub>18</sub> carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ammonium alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C<sub>11-13</sub> LAS.

Preferred nonionic surfactants are those of the formula R<sup>1</sup>(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, wherein R<sup>1</sup> is a C<sub>10</sub>-C<sub>16</sub> alkyl group or a C<sub>8</sub>-C<sub>12</sub> alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C<sub>12</sub>-C<sub>15</sub> alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C<sub>12</sub>-C<sub>13</sub> alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:



wherein R is a C9-17 alkyl or alkenyl, R<sub>1</sub> is a methyl group and Z is glycetyl derived from a reduced sugar or alkoxyLATED derivative thereof. Examples are N-methyl N-1-deoxyglucyl cocoamide and N-methyl N-1-deoxyglucyl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

B) Detergent Builder

The detergent compositions herein also essentially comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al. and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and

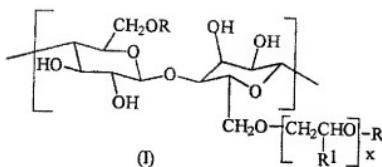
silicates having a weight ratio of SiO<sub>2</sub> to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al, U. S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also, crystalline layered silicates such as those discussed in Corkill et al, U. S. Patent No. 4,605,509, incorporated herein by reference, are suitable for use in the detergent compositions of this invention.

### C) Modified Cellulosic Polymers

The third essential component of the detergent compositions herein comprises one or more modified cellulosic polymers. Such materials have been found to impart a number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such modified cellulosic materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, etc. The modified cellulosic polymers used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

The modified cellulosic polymers useful herein may be of the nonionic, cationic or anionic types, or the modified cellulosic polymeric component of the compositions herein may comprise combinations of these cellulosic polymer types. The modified cellulosic polymer component of the compositions herein will generally comprise from about 0.1% to 8% by the weight of the composition. More preferably, such modified cellulosic materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%.

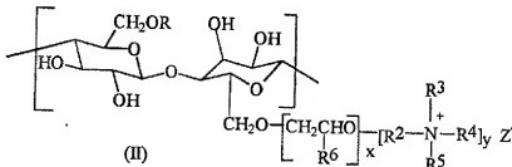
One suitable type of modified cellulosic polymer for use herein comprises hydrophobically-modified, nonionic cellulose ethers having a molecular weight of from about 10,000 to 2,000,000, preferably from about 50,000 to 1,000,000. The hydrophobically-modified nonionic materials have repeating, substituted anhydroglucoside units which correspond to the general Structural Formula No. I as follows:

Structural Formula No. I

In Structural Formula No. I, R is a combination of H and C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. Alkyl substitution on the anhydroglucoside rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymer material. Also, in Structural Formula No. I, R<sup>1</sup> is H or methyl, and x ranges from about 1 to 20, preferably from about 1 to 10.

The hydrophobically-modified nonionic cellulose ethers of Structural Formula No. I include those which are commercially available and also include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. I type include Polysurf 67, Natrosol Plus 430 and Natrosol Plus 330, all marketed by Hercules, Inc.

Another suitable type of modified cellulosic polymer for use herein comprises certain cationic cellulose ethers, which may or may not be hydrophobically-modified, having a molecular weight of from about 10,000 to 2,000,000, more preferably from about 10,000 to 1,000,000. These cationic materials have repeating substituted anhydroglucoside units which correspond to the general Structural Formula No. II as follows:

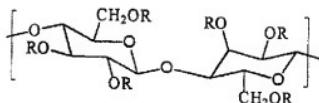


Structural Formula No. II

In Structural Formula No. II, R is H or C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. Alkyl substitution on the anhydroglucose rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymeric material. Also, in Structural Formula No. II, R<sup>2</sup> is CH<sub>2</sub>CHOHCH<sub>2</sub> or C<sub>8</sub>-C<sub>24</sub> alkyl, preferably C<sub>8</sub> - C<sub>16</sub> alkyl. R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently methyl, ethyl or phenyl. R<sup>6</sup> is H or methyl. Further, in Structural Formula No. II, x ranges from about 1 to 20, preferably from about 1 to 10; and y ranges from about 0.005 to 0.5, preferably from about 0.005 to 0.1; and Z is Cl<sup>-</sup> or Br<sup>-</sup>.

The cationic cellulose ethers of Structural Formula No. II likewise include those which are commercially available and further include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. II type include the JR 30M, JR 400, JR 125, LR 400 and LK 400 UCARE polymers, all marketed by Union Carbide Corporation.

A third type of suitable modified cellulose polymers for use herein comprises certain anionic cellulose ethers, which also may or may not be hydrophobically-modified, having a molecular weight of from about 10,000 to 2,000,000, more preferably from about 50,000 to 1,000,000. These anionic materials have repeating substituted anhydroglucose units which correspond to general Structural Formula No. III as follows:

Structural Formula No. III

In Structural Formula No. III, R is a combination of H and a) CH<sub>2</sub>COOA and, optionally, b) C<sub>2</sub>-C<sub>24</sub>, preferably C<sub>2</sub> - C<sub>16</sub>, alkyl, with A being Na or K. Alkyl substitution on the anhydroglucose rings of the polymer ranges from about 0.1% to 5% by weight, more preferably from about 0.2% to 2% by weight, of the polymer material. The anionic cellulose ethers also have a degree of carboxymethyl

substitution which ranges from about 0.05 to 2.5, more preferably from about 0.1 to 1.0.

The anionic cellulose ethers of Structural Formula No. III also include those materials which are commercially available and further include those which can be prepared by conventional chemical modification of commercially available materials. Commercially available cellulose ethers of the Structural Formula No. III include CMC 7H, CMC 99-7M and CMC 99-7L, all marketed by Hercules, Inc. and CMC D72, CMC D65 and CMC DHT, all marketed by Penn Carbose.

The commercially available cellulose ether materials useful herein are themselves derived from suitable natural sources of cellulose. Such sources include, for example, cotton linters and other vegetable tissues. The modified cellulose ethers used in this invention are generally all water-soluble materials. They can therefore be utilized for detergent composition preparation in the form of aqueous solutions of the such cellulosic polymers if desired.

#### D) Optional Detergent Ingredients

In addition to the essential surfactants, builders and modified cellose ethers hereinbefore described, the detergent composition of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as bleaches and bleach activators, enzymes and enzyme stabilizing agents, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, organic and inorganic fillers, solvents, hydrotropes, optical brighteners, dyes and perfumes.

A preferred optional ingredients for incorporation into the detergent compositions herein comprises a bleaching agent, e.g., a peroxygen bleach. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

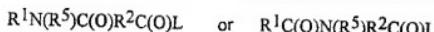
Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published

February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used, generally in particulate form, in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials. For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interrox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical and preferred. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

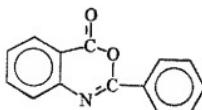
Other useful amido-derived bleach activators are those of the formulae:



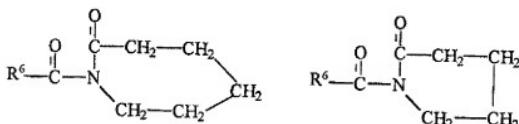
wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonenamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966,723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, nonanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If utilized, peroxygen bleaching agent will generally comprise from about 2% to 30% by weight of the detergent compositions herein. More preferably, peroxygen bleaching agent will comprise from about 2% to 20% by weight of the compositions. Most preferably, peroxygen bleaching agent will be present to the extent of from about 3% to 15% by weight of the compositions herein. If utilized, bleach activators can comprise from about 2% to 10% by weight of the detergent compositions herein.

Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

Another highly preferred optional ingredient in the detergent compositions herein is a detergents enzymes component. Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases, amylases and peroxidases.

Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-

Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 10. U.S. 4,435,307, Barbesgaard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lamiginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein.

The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergents enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a

manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

#### E) Detergent Composition Preparation

The detergent compositions according to the present invention can be in liquid, paste or granular forms. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients (e.g. surfactants, builders, water, etc.) as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients can be admixed in granular powder form with the spray dried granules in a rotary mixing drum and the liquid ingredients (e.g. organic solutions of the essential cellulosic polymers, enzymes, binders and perfumes) can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Addition of the cellulose ether component to liquid detergent compositions of this invention may be accomplished by simply mixing into the liquid detergent aqueous solutions of the desired cellulose ethers. Cellulose ethers can alter the viscosity or other rheological characteristics of liquid detergent products. It may

therefore be necessary to compensate for any rheological changes in the liquid detergent product brought about by cellulose ether addition by altering the type and amount of hydrotropes and/or solvents that are used.

#### F) Fabric Laundering Method

The present invention also provides a method for laundering fabrics in a manner which imparts fabric appearance benefits provided by the cellulosic polymers used herein. Such a method employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described or formed from the individual components of such compositions. Contacting of fabrics with washing solution will generally occur under conditions of agitation although the compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment.

Agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective amount of the liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 7000 ppm, more preferably from about 1000 to about 3000 ppm.

#### G) Fabric Conditioning

The modified cellulose ethers hereinbefore described as components of the laundry detergent compositions herein may also be used to treat and condition fabrics and textiles in the absence of the surfactant and builder components of the detergent composition embodiments of this invention. Thus, for example, a fabric conditioning composition comprising only the modified cellulose ethers themselves, or comprising an aqueous solution of the modified cellulose ethers, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described.

### EXAMPLES

The following examples illustrate the compositions and methods of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

EXAMPLE I  
Liquid Detergent Test Composition Preparation

Several heavy duty liquid detergent compositions are prepared containing various modified cellulosic polymers. Such liquid detergent compositions all have the following basic formula:

Table A

<u>Component</u>	<u>Wt. %</u>
C <sub>12</sub> -15 alkyl ether (2.5) sulfate	38
C <sub>12</sub> glucose amide	6.86
Citric Acid	4.75
C <sub>12</sub> -14 Fatty Acid	2.00
Enzymes	1.02
MEA	1.0
Propanediol	0.36
Borax	6.58
Dispersant	1.48
Na Toluene Sulfonate	6.25
Modified Cellulosic Polymer (if present)	2.0
Dye, Perfume, Brighteners, Preservatives, Suds Suppressor, Other Minors, Water	<u>Balance</u>
	100%

**EXAMPLE II**  
**Granular Detergent Test Composition Preparation**

Several heavy duty granular detergent compositions are prepared containing various modified cellulosic polymers. Such granular detergent compositions all have the following basic formula:

**Table B**

<u>Component</u>	<u>Wt. %</u>
C <sub>12</sub> Linear alkyl benzene sulfonate	9.31
C <sub>14-15</sub> alkyl ether (0.35 EO) sulfate	12.74
Zeolite Builder	27.79
Sodium Carbonate	27.31
PEG 4000	1.60
Dispersant	2.26
C <sub>12-13</sub> Alcohol Ethoxylate (9 EO)	1.5
Sodium Perborate	1.03
Soil Release Polymer	0.41
Enzymes	0.59
Modified Cellulosic Polymer (if present)	2.5
Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate	<u>Balance</u>
	100%

**EXAMPLE III**  
**Cellulosic Polymers Used in Test Compositions**

The representative modified cellulosic polymers used in the liquid and granular detergent compositions described in Examples I and II are characterized in Table C. The various substituents listed are those from Structural Formulas Nos. I, II and III described hereinbefore.

**Table C**  
**Cellulosic Polymers Used in Test Detergent Compositions**

<u>Polymer Description</u>	<u>Polymer ID</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Polymer Tradename	Polysurf 67	LK-400	CMC (D72)	Modified LK-400
Polymer Manufacturer	Hercules	Union Carbide	Penn Carbose	Union Carbide
Polymer Type	Nonionic	Cationic	Anionic	Cationic
Molecular Weight	700-750M	~400M	~300M	~400M
Structure No.	I	II	III	II
R	Cetyl (C <sub>16</sub> )	H	CH <sub>2</sub> COO	H
Amount of Ring Alkyl Substitution	0.4% 0.6%	0	0	0
Degree of Ring Carboxymethyl Substitution	-	-	0.5	-
R <sup>1</sup>	H	-	-	-
R <sup>2</sup>	-	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> -	-	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> -
R <sup>3</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>4</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>5</sup>	-	-CH <sub>3</sub>	-	-CH <sub>3</sub>
R <sup>6</sup>	-	H	-	H
x	1-3	1-3	-	1-3
y	-	~0.1	-	~0.006
Z	-	Cl <sup>-</sup>	-	Cl <sup>-</sup>
A	-	-	Na	-

Test compositions prepared as described in Examples I and II are evaluated for the effects that the various cellulosic polymers of Example III provide when samples of fabrics or garments are washed using the test compositions as described, all under identical conditions. A control sample with no polymer is usually compared to one composition with a test polymer to be evaluated. Testing conditions are also carefully monitored. Examples of controlled conditions include: wash time, wash

water temperature and hardness; washer agitation; rinse time, rinse water temperature and hardness; dryer time and temperature; wash load fiber content and weight.

#### EXAMPLE IV

##### Overall Appearance

In an **Overall Appearance** test, fabrics are washed using various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed after ten cycles are then comparatively graded by three judges who evaluate the overall appearance of the washed fabrics. It is the decision of the judge as to what is to be evaluated unless specific direction is given to evaluate one attribute such as color, pilling, fuzz, etc.

In the **Overall Appearance** test, the visual preference of the judge is expressed using the Scheff scale.

- That is:
- 0 = No difference
  - 1 = I think this one is better (unsure).
  - 2 = I know this one is a little better.
  - 3 = I know this one is a lot better.
  - 4 = I know this one is a whole lot better.

For the **Overall Appearance** test, laundering conditions are as follows:

Washer Type: Kenmore (17 gallons)

Wash Time: 12 min

Wash Temperature: 90°F (32.2°C)

Wash Water Hardness: 6 grains per gallon

Washer Agitation: normal

Rinse Time: 2 min

Rinse Temperature: 60°F (15.6°C)

Rinse Water Hardness: 6 grains per gallon

Wash Load Fabric Content: various colored and white garments and  
fabrics

Wash Load Weight: 5.5 lbs (2.5 kg)

The average overall appearance test results are shown in Tables D and E.

Table D  
Overall Appearance Test Results

Liquid Test Composition ID	Polymer Tested	Overall Appearance Grade
Control	None	0
A	Polysurf 67	1.5
B	LK-400	1.8
C	CMC (D72)	1.0
D	Modified LK-400	1.2

Table E  
Overall Appearance Test Results

Granular Test Composition ID	Polymer Tested	Overall Appearance Grade
Control	None	0
A	Polysurf 67	1.4
B	LK-400	1.0
C	CMC (D72)	1.0
D	Modified LK-400	1.1

EXAMPLE V  
Pill Reduction

In a Pill Reduction test, fabrics are washed using the various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed are then graded for Pill Reduction using a computer-assisted pilling image analysis system which employs image analysis to measure the number of pills on tested garments and fabrics. Pill reduction is calculated as:

$$\text{Pill reduction(%)} = \{ [\# \text{ pills (control)} - \# \text{ pills (polymers)}] / \# \text{ pills (control)} \} \times 100\%$$

For the Pill Reduction test, laundering conditions are the same as used for the Overall Appearance test described hereinbefore in Example IV.

The average % Pill Reduction test results are shown in Tables F and G.

Table F  
Pill Reduction Test Results - Liquids

<u>Liquid Test Composition ID</u>	<u>Polymer Tested</u>	<u>Pill/Fuzz Reduction (%)</u>
Control	None	0
A	Polysurf 67	21.5
B	LK-400	42.4
C	CMC(D72)	26.8
D	Modified LK-400	25.9

Table G  
Pill Reduction Test Results - Granular

<u>Granular Test Composition ID</u>	<u>Polymer Tested</u>	<u>Pill/Fuzz Reduction (%)</u>
Control	None	
A	Polysurf 67	33.3
B	LK-400	51.6
C	CMC(D72)	7.6
D	Modified LK-400	16.6

**EXAMPLE VI**  
**Color Protection**

In a **Color Protection** test, fabrics are washed using various test compositions containing either no cellulosic polymers or one of the Example III cellulosic polymers. The fabrics so washed are then tested with a Hunter colorimeter in order to determine a Delta E\* value for each fabric tested. Delta E\* is defined as the color difference (reflectance intensity, hue shift, etc.) between washed fabrics and unwashed fabrics.

For the **Color Protection** test, laundering conditions are the same as used for the **Overall Appearance** test described hereinbefore in Example IV.

The extent of **Color Protection** provided is based on percent of Delta E\* difference compared to an unwashed sample. Color protection is calculated as:

$$\% \text{ Color Protection} = \{ [dE^*(\text{control}) - dE^*(\text{polymers})] / dE^*(\text{control}) \} \times 100\%$$

The average color protection test results are shown in Tables H and I.

**Table H**  
**Color Protection Test Results - Liquids**

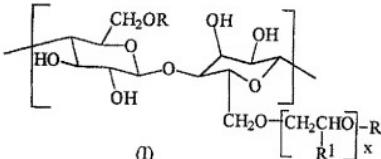
<u>Liquid Test Composition ID</u>	<u>Polymer Tested</u>	<u>Color Protection (%)</u>
Control	None	0
A	Polysurf 67	24.2
B	LK-400	36.5
C	CMC (D72)	26.6
D	Modified LK-400	27.2

Table I  
Color Protection Test Results - Granular

<u>Granular Test Composition</u>	<u>Polymer Tested</u>	<u>Color Protection (%)</u>
<u>ID</u>		
Control	None	0
A	Polysurf 67	33.9
B	LK-400	39.2
C	CMC (D72)	15.5
D	Modified LK-400	24.7

What is claimed is:

- I. A laundry detergent composition which imparts fabric appearance benefits selected from pill/fuzz reduction, antifading, improved abrasion resistance and/or enhanced softness to fabrics and textiles laundered in aqueous washing solutions formed therefrom, which composition is characterized by:
  - A) from 1% to 80% by weight of a detergents surfactant;
  - B) from 0.1% to 80% by weight of an organic or inorganic detergency builder;
  - C) from 0.1% to 8% by weight of a modified cellulose ether fabric treatment agent selected from the group consisting of:
    - i) hydrophobically-modified, nonionic cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:



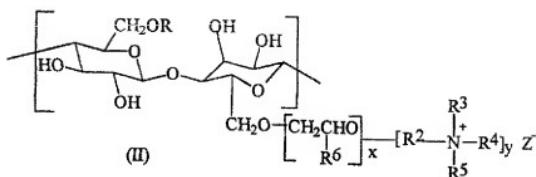
wherein:

R is a combination of H and C<sub>8</sub>-C<sub>24</sub> with alkyl substitution of the anhydroglucose rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material;

R<sup>1</sup> is H or methyl; and

x ranges from 1 to 20;

- ii) cationic quaternary ammonium cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:



wherein:

R is H or C<sub>8</sub>-24, with alkyl substitution of the anhydroglucoside rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material;

R<sub>2</sub> is CH<sub>2</sub>CHOHCH<sub>2</sub> or C<sub>8</sub>-24 alkyl;

R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each, independently, methyl, ethyl or phenyl;

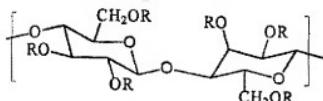
R<sub>6</sub> is H or methyl;

x ranges from 1 to 20;

y ranges from 0.005 to 0.5; and

Z is Cl<sup>-</sup> or Br<sup>-</sup>;

- iii) anionic cellulose ethers which have a molecular weight of from 10,000 to 2,000,000 and which have repeating substituted anhydroglucose units corresponding to the general formula:



wherein:

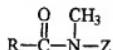
R is a combination of H and a) CH<sub>2</sub>COOA, and, optionally, b) C<sub>8</sub>-24 alkyl, with alkyl substitution of the anhydroglucoside rings ranging in an amount of from 0.1% to 5% by weight of the cellulose ether material, and with the degree of carboxymethyl substitution of the anhydroglucose rings ranging from 0.05 to 2.5; and wherein A is Na or K; and

- iv) combinations of said nonionic, cationic and anionic cellulose ethers.

2. A composition according to Claim 1 wherein
  - A) the deterotive surfactant comprises from 5% to 50% by weight and is selected from anionic and nonionic surfactant materials
  - B) the detergency builder is characterized by from 10% to 50% by weight and is selected from carboxylates, silicates, aluminosilicates, carbonates, borates and combinations thereof; and
  - C) the modified cellulose ether fabric treatment agents comprises from 0.5% to 4% by weight and have molecular weights ranging from 10,000 to 1,000,000.
3. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is a hydrophobically-modified, nonionic material corresponding to Structural Formula No. I wherein
  - a) R is a combination of H and C<sub>8</sub> to C<sub>16</sub> alkyl;
  - b) R substitution of the anhydroglucose rings ranges from 0.2% to 2% by weight of the cellulose ether;
  - c) R<sup>1</sup> is H; and
  - d) x ranges from 1 to 10.
4. A composition according to Claim 3 wherein the hydrophobically-modified, nonionic cellulose ether is selected from Polysurf 67, Natrosol Plus 430 and Natrosol Plus 330.
5. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is a cationic material corresponding to Structural Formula No. II wherein
  - a) R is C<sub>8</sub> to C<sub>16</sub> alkyl;
  - b) R substitution of the anhydroglucose rings ranges from 0.2% to 2% by weight of the cellulose ether;
  - c) R<sup>2</sup> is C<sub>8</sub> to C<sub>16</sub> alkyl or is CH<sub>2</sub>CH(OH)CH<sub>2</sub>;
  - d) R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each methyl;
  - e) R<sup>6</sup> is H;

- f) x ranges from 1 to 10;
  - g) y ranges from 0.005 to 0.1; and
  - h) Z is Cl<sup>-</sup>.
6. A composition according to Claim 5 wherein the cationic cellulose ether is selected from UCARE JR 30M, JR 400, JR 125, LR 400 and LK 400 and derivatives thereof.
7. A composition according to Claim 2 wherein the modified cellulose ether fabric treatment agent is an anionic material corresponding to Structural Formula No. III wherein:
- a) R is optionally C<sub>8</sub> to C<sub>16</sub> alkyl;
  - b) R substitution of the anhydroglucoside rings ranges from 0.2% to 2% by weight of the cellulose ether;
  - c) the degree of carboxymethyl substitution ranges from 0.1 to 1.0; and
  - d) A is Na.
8. A composition according to Claim 7 wherein the anionic cellulose ether is selected from CMC 7H, CMC 99-7M, CMC 99-7L, CMC D72, CMC D65 and CMC DHT.
9. A composition according to Claim 2 in liquid form which is characterized by:

- a) from 5% to 50% by weight of a detergentsurfactant selected from
  - i) sodium, potassium and ammonium alkylsulfates wherein the alkyl group contains from 10 to 22 carbon atoms;
  - ii) sodium, potassium and ammonium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;
  - iii) polyhydroxy fatty acid amides of the formula



wherein R is a C<sub>9-17</sub> alkyl or alkenyl and Z is glycidyl derived from a reduced sugar or alkoxylated derivatives thereof,

- iv) alcohol ethoxylates of the formula  $R^1(OC_2H_4)_nOH$  wherein  $R^1$  is a  $C_{10}$ - $C_{16}$  alkyl group or a  $C_8$ - $C_{12}$  alkyl phenyl group and n is from 3 to 80; and
  - v) combinations of these surfactants; and
- b) from 1% to 10% by weight of a detergent builder component selected from carboxylate and polycarboxylate builders.
10. A composition according to Claim 2 in granular form which is characterized by:
- a) from 5% to 50% by weight of a detergentsurfactant selected from
    - i) sodium and potassium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;
    - ii) sodium and potassium  $C_9$  to  $C_{15}$  alkyl benzene sulfonates;
    - iii) sodium and potassium  $C_8$  to  $C_{18}$  alkyl sulfates;
    - iv) polyhydroxy fatty acid amides of the formula
- $$\begin{array}{c} O \quad CH_3 \\ || \quad | \\ R-C-N-Z \end{array}$$
- wherein R is a  $C_{9-17}$  alkyl or alketyl and Z is glycyld derived from a reduced sugar or alkoxylated derivatives thereof; and
- v) combinations of these surfactants; and
- b) from 1% to 50% by weight of a detergent builder selected from sodium carbonate, sodium silicate, crystalline layered silicates, aluminosilicates, oxydisuccinates and citrates;



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(54) Title: <b>LAUNDRY DETERGENT COMPOSITIONS WITH CELLULOLOSIC POLYMERS</b>			
(57) Abstract			
<p>Disclosed are detergent compositions and methods which utilize certain modified cellulose ethers as fabric treatment agents that can impart fabric appearance and integrity benefits to fabrics and textiles laundered in washing solutions which contain such agents. Such modified cellulose ether fabric treatment agents are those having selected types and amounts of anhydroglucoside ring substituents in order to render them nonionic, cationic or anionic in nature.</p>			

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## INTERNATIONAL SEARCH REPORT

In International Application No  
PCT/US 97/23771

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/22 C11D3/382 //C11D1/12,C11D1/29,C11D1/66

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	EP 0 634 481 A (PROCTER & GAMBLE) 18 January 1995 see page 10, line 20 - line 23 see examples A-D ---	1,2,7,8, 10
X	US 4 329 237 A (WIXON HAROLD E) 11 May 1982 see claims 1,25 see column 3, line 4 - line 9 ---	1,2,7,8, 10
X	US 3 950 276 A (GRAND PAUL SHELDON) 13 April 1976 see claims 1-5 see example 8 ---	1,2,7,8
X	EP 0 279 040 A (DEGUSSA) 24 August 1988 see claim 1 ---	1,2,7
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "U" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"V" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"G" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 1998	15/07/1998
Name and mailing address of the ISA European Patent Office, P.B. 5016 Patentaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx 31 651 esp n. Fax: (+31-70) 340-3016	Authorized officer  Richards, M

## INTERNATIONAL SEARCH REPORT

International Application No

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A	WO 95 00614 A (KAO CORP ; SAKATA YUSHI (JP); TAMURA YUMIKO (JP); INOKOSHI JUNICHI) 5 January 1995 see claims 1-20 see page 24, line 11 - page 25, line 3 see table 2 -----	1,2,5,6, 9,10
P,A	WO 97 20020 A (UNILEVER NV ; UNILEVER PLC (GB)) 5 June 1997 see claims 1-9 -----	1,2,7,8
A	US 5 540 850 A (FOSTER FRANCIS G) 30 July 1996 see claims 1-3 -----	1,2

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